

**CHEMICAL AND SEM STUDIES OF MINERAL ASSEMBLAGES WITHIN ALH84001.** C. N. Foley<sup>1</sup>, M. Humayun<sup>1</sup>, A. M. Davis<sup>1,2</sup>, O. Kagan<sup>1</sup>, <sup>1</sup>Department of Geophysical Sciences, <sup>2</sup>Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637, USA. Email: nfoley@geosci.uchicago.edu

ALH84001 is an ancient Martian meteorite which contains carbonate globules and other minerals derived from a fluid extraneous to the orthopyroxenite rock of which it is largely constituted. McKay et al. [1] reported nanometer-sized features interpreted as possible fossilized bacteria from these carbonate globules, and other evidences of "possible relic biogenic activity". This meteorite has come under intense scrutiny, and studies of temperature of formation, S isotopes, etc. [2, 3, 4, 5, 9] have revealed the complexities of both the origin of the globules and the possible clues to ancient life on Mars.

We are carrying out a trace element study of the ALH84001 meteorite to investigate possible biomineralization, and to search for clues to the origin of the carbonate assemblage. Prior to destructive analysis, we are conducting a careful SEM examination of three chips, each 1-2g in size, to obtain information regarding the petrographic relations of carbonates to other minerals in the rock. This enables us to compare the materials we separate for analysis with literature reports and guides our selection of materials for analysis. Since our studies were carried out on chips, without polishing or coating, we were examining fracture surfaces. Our findings were often different from those reported in the literature. This we attribute to the presence of a distinction between carbonates exposed on fracture surfaces, and those intersected by thin-sectioning. This distinction may explain differences observed between various reports [1, 6, 7, 9].

The SEM used in this study is a JEOL JSM5800LV equipped with an Oxford Link ISIS-300 x-ray analysis system. We have investigated two interior chips and an exterior chip of ALH84001 by SEM using a low-vacuum mode that allows direct imaging and x-ray analysis of the fractured surfaces without polishing or coating the samples.

The fracture faces we observed were induced by curatorial activity at JSC, but the sample probably fractured along pre-existing weaknesses, including some induced on Earth during residence in the Antarctic ice. Our studies of the chip surfaces revealed faces that exposed preexisting fractures covered with carbonate globules, as well as fractures bearing few or no carbonates.

The exterior chip we have examined (.265) is partially covered by fusion crust. It has one 8mm x 4mm fracture face almost entirely covered with carbonate globules, while the remaining surfaces are

sparsely covered by globules. An interior chip (.261a) has a single face covered with over a hundred individual globules, and again, few globules on the other surfaces. X-ray mosaic maps revealed the distribution of the minerals present on the fracture surfaces.

We observed gradual chemical zonation of the carbonate globules on the .265 fracture surface similar to those reported by others [e.g. 6,7], which we will term here type 1 carbonate globules. The general pattern of zonation is a central core rich in Ca (up to 20 mol% calcite) surrounded by a region of increasing Mg content followed by three sharp bands of sideritic, magnesitic, and ankeritic carbonate (Fig. 1 a,b). In type 1 carbonates, the sulfur contents of the ankeritic rims are detectable above analytical limits at about  $0.25 \pm 0.05$  wt% ( $2\sigma$ ), while no sulfur is detectable in the interior carbonate, i.e.  $<0.1$  wt%. In .261a the particular face covered with over a hundred carbonate globules revealed both type 1 and type 2 globules. These later globules are characterized by having Fe sulfide blebs, with S contents up to 8 wt% of the bulk globule. These globules comprise  $\approx 10\%$  (by number) of the carbonate abundance on this fracture surface. A detailed analysis of one of these globules revealed that the  $\approx 0.1$   $\mu\text{m}$  Fe sulfide blebs were located in a distinct pattern, following the rhombohedral cleavage exhibited by the globule interior (Fig. 2). In reflected light, type 1 carbonates show an orange interior [1], surrounded by light magnesite and dark Fe-carbonate bands. The type 2 globules have a dark interior instead. This is due to the presence of numerous tiny sulfide blebs. These globules will be targeted for future S isotopic and chemical studies.

Both features of the sulfide in type 2 carbonates, the localization along cleavage traces and the zonally asymmetric distribution, imply that these sulfides were introduced into the globules after crystallization of the carbonate cores. We tentatively conclude that such sulfides may have been shock emplaced from a sulfide melt derived from local sulfide minerals, perhaps during the same impact event that emplaced the shock-melted maskelynitic glass [8].

The mosaics further reveal that Fe sulfides occur as grains of  $\leq 10\mu\text{m}$  in elongated bands associated with crushed zones (granular bands). No Fe sulfides found appear to be part of the original igneous assemblage of the rock, which consists of opx+chr+mask+Ca-phosphate. This was remarked upon by Greenwood et al. [4], and we confirm their observation, within the

## SEM STUDIES OF ALH84001: Foley et al.

limits imposed by the material available for study. The implications of this finding are that sulfide and carbonates are cogenetic, as recognized previously [6, 7]. Therefore, the similar  $\delta^{34}\text{S}$  observed in sulfides from carbonate globules and  $\approx 10\ \mu\text{m}$  grains in the crushed zones is the expected result [4, 5, 9]. Our observations imply that both sulfides within globules and those in the matrix share the same origin, biogenic or otherwise. Perhaps the most significant sulfur isotopic observation is that these sulfides are heavier in  $\delta^{34}\text{S}$  than pyrrhotites in the shergottites [9].

No direct association is found between maskelynitic glass and the carbonate globules, which are mainly underlain by opx. It has been proposed that ALH84001 carbonates formed by replacement of maskelynitic glasses [6,7], and this has important implications for the Rb-Sr geochronology of these minerals [10]. We observe carbonate globules largely on opx surfaces, with only sporadic association with maskelynitic glass, which appear to be coincidental. Like McKay et al. [1], we are studying mineral associations on fracture surfaces. Numerous observations of carbonate with maskelynitic glasses have been reported from thin section studies, which indicate one of the important differences between globules in fracture surfaces and those found in thin section.

**Conclusions:** We find zoned carbonate globules on fracture surfaces consisting of two types, differentiated by the latter having Fe sulfide blebs, with S contents of up to 8 wt%. Sulfides occur in the interior of carbonate globules (type 2), in the Fe-rims of the globules (type 1, 2), and as individual grains up to  $\approx 10\ \mu\text{m}$  in size in the crushed zones. No sulfide has been found in association with magmatic minerals. We find no evidence to support a replacement origin of the carbonates by alteration of feldspathic glasses. The fundamental issues of the origin of the globules remain unknown.

**REFERENCES:** [1] McKay D. S. et al. (1996) *Science*, 273, 924-929. [2] Romanek, C. S. et al. (1994) *Nature*, 372, 655-657. [3] Harvey R. P. and McSween H. Y., Jr. (1996) *Nature*, 382, 49-51. [4] Greenwood J. P. et al. (1997) *Geochim. Cosmochim. Acta.*, 61, 4449-4453. [5] Shearer C. K. et al., (1996) *Geochim. Cosmochim. Acta.*, 60, 2921-2926. [6] Mittlefehldt D. W. (1994) *Meteoritics*, 29, 214-221. [7] Treiman A. H. (1995) *Meteoritics*, 30, 294-302. [8] Scott et al. (1997) *Nature* 387, 377-379. [9] Boctor et al. (1998) *LPSC XXIX*, this volume. [10] Wadhwa M. and Lugmair G. W. (1996) *Meteoritics*, 31, A145.

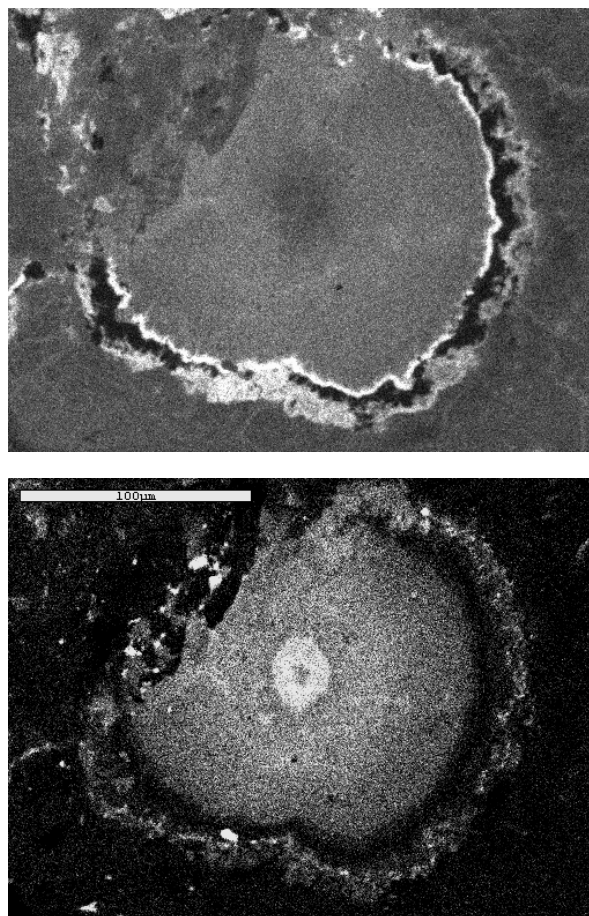


Figure 1: a) Fe X-ray map (above). Fe rich zones are bright. Fe rich sideritic inner rim and outer ankeritic rim are clearly illustrated. b) Ca X-ray map (below). Ca rich zones are bright. Ca rich inner zoned core and ankeritic outer rim are visible. Scale bar= 100  $\mu\text{m}$ .

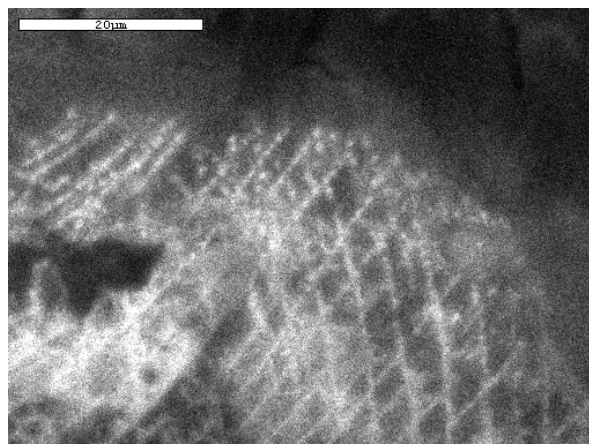


Figure 3: S X-ray map of a portion of a type 2 globule. Finely dispersed Fe sulfide blebs  $\approx 0.1\ \mu\text{m}$  in diameter occur along cleavage planes of the carbonate interior. Scale bar=20  $\mu\text{m}$ .